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Fully automated on-line headspace monitoring of VOCs from waste effluent by GC–FID and GC–TOF MS

This study demonstrates a fully automated GC analysis of volatile organic compounds (VOCs) in the headspace of waste effluent using a flow-through cell with a sample preparation robot, and detection by FID and/or TOF MS. The use of these two detection techniques enables robust on-line quantitation of target compounds, as well as confident identification of unknowns and emerging contaminants.

Introduction

Environmental agencies regularly monitor watercourses and coastal waters for the presence of a variety of compound classes, to ensure that any releases from industry are within acceptable limits. To reduce the risk of fines (or even site closure), manual spot-checks have commonly been used by companies to monitor their own releases, but the lowering of limit levels means that these are no longer adequate, and run the risk of missing pollution events.

This has increased the need for fully automated, continuous monitoring at multiple monitoring points, employing robust sampling and quantitation procedures, and in-field analysis by non-specialists. If detected, any sources of contamination must also be localised, which requires robust mass-spectrometric identification of unknowns and/or emerging contaminants.

In this study, we employ a flow-through cell for on-line effluent sampling, in conjunction with robotic tool change for time-efficient sampling, standard addition and headspace analysis on a single, fully-automated platform. The use of GC–FID for analysis enables remote, continuous monitoring for rapid response to contamination events, while GC–TOF MS provides confirmatory analysis and identification of unknowns or compounds of emerging concern.

Experimental

Method validation was performed on two systems, one using FID and the other using TOF MS.

Samples: A calibration series of 28 VOC standards, ranging in volatility from dimethyl ether to bromoform and substituted benzenes, were prepared at 0.5–20 µg/mL (FID) and 0.5–20 ng/mL (TOF MS). The requirement to monitor methanol, coupled with the availability of many analytes only as solutions in methanol, necessitated that two calibration mixes were used for development and validation: (A) using water as solvent, for acetaldehyde, methanol, acetone, isopropanol and *tert*-butanol; (B) using methanol as solvent, for all other analytes.

On-line sampling: A Sample Preparation Robot (SepSolve Analytical) was used to sample 15 mL of water from a flow-through cell to a headspace vial, prior to spiking with standards (Figure 1).

GC: Instrument: Agilent 7890B fitted with a Sample Preparation Robot.

FID: H_2 flow: 30 mL/min; Air flow: 300 mL/min; Temperature: 300°C; Makeup: 5 mL/min.

MS: Instrument: BenchTOF-Select™ time-of-flight mass spectrometer (Markes International); Transfer line: 260°C; Ion source: 260°C; Ionisation energy: 70 eV.

Software: TOF-DS™ software for full instrument control and data processing.

Please contact SepSolve for full analytical parameters.

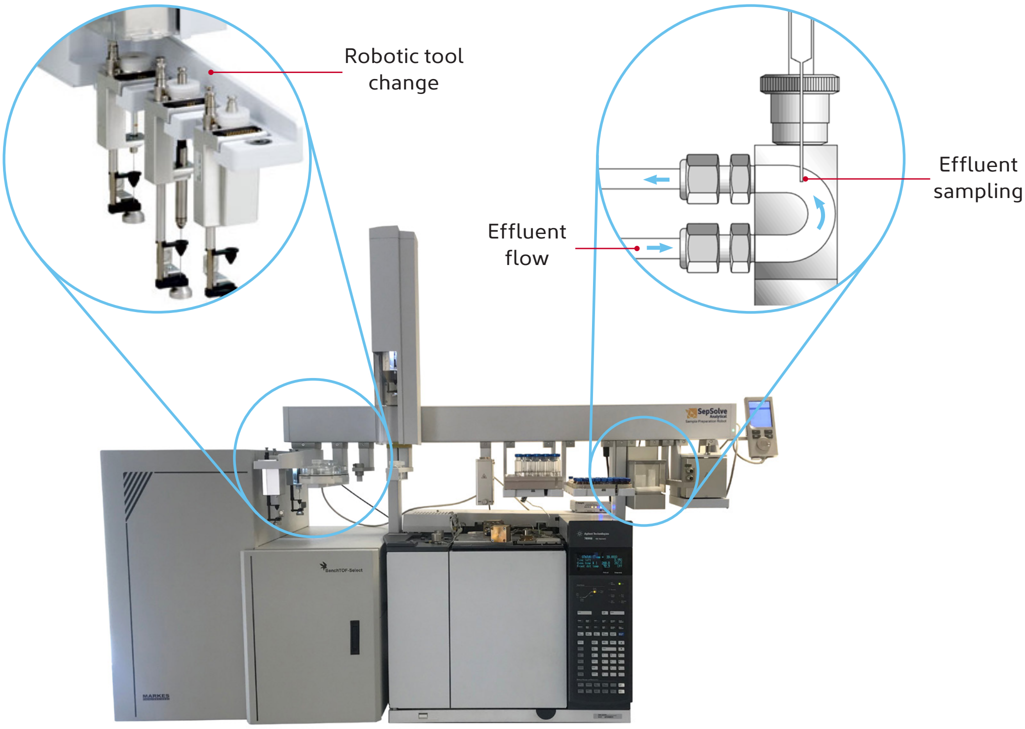


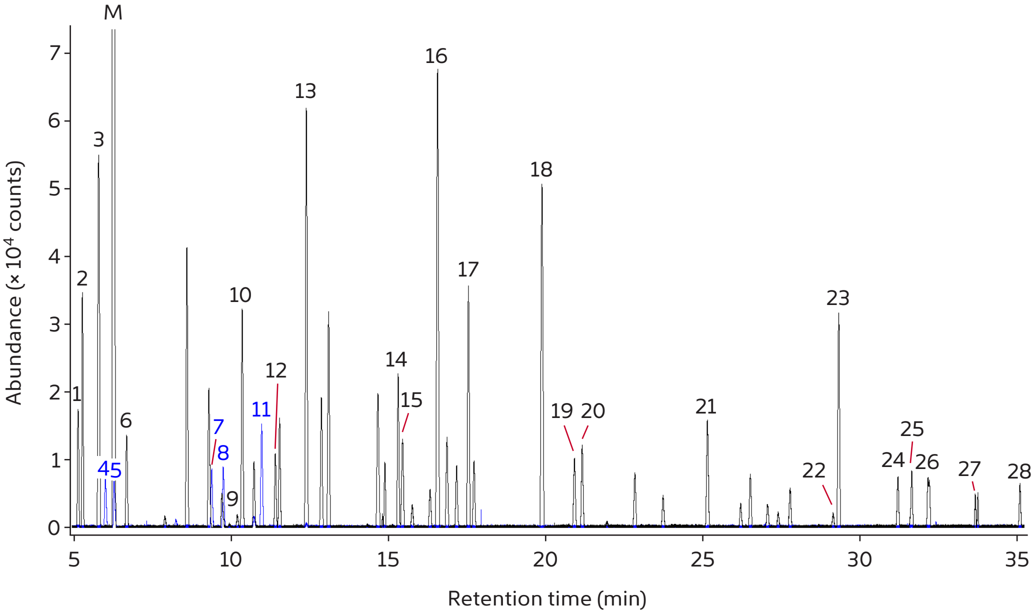
Figure 1

GC–FID/TOF MS system used in this study, with robotic tool change and flow cell highlighted on the sample preparation robot.

Results and discussion

1. Separation of target analytes

The wide range of compound classes that may be present in effluent demands excellent resolution to ensure confidence in identification. Figure 2 shows an overlay of the two analyte mixes analysed at the method detection limit (MDL) required in this particular case, and demonstrates baseline separation of all target compounds.



1	Dimethyl ether	11	*tert*-Butanol	21	Toluene
2	Chloromethane	12	Acrylonitrile	22	Dibromochloromethane
3	Butadiene	13	n-Hexane	23	4-Vinylcyclohexene (Butadiene dimer)
4	Acetaldehyde	14	Bromochloromethane	24	Chlorobenzene
5	Methanol	15	Chloroform	25	Ethylbenzene
6	Bromomethane	16	Cyclohexane	26	*m*- + *p*-Xylene
7	Acetone	17	Benzene	27	Styrene
8	Isopropanol	18	2,4,4-Trimethylpent-1-ene	28	Bromoform
9	Acetonitrile	19	Dibromomethane		
10	Dichloromethane	20	Bromodichloromethane		

Figure 2

Overlaid GC–FID chromatograms showing detection of target compounds for the two standard mixes (Mix A – blue trace, Mix B – black trace) at the MDL required in this particular case (0.5 µg/mL). Unlabelled peaks were not target analytes for this study.
M = Methanol solvent.

2. Linearity

External calibration curves, based on absolute area, were prepared using TOF-DS™ for all target VOCs at 0.5–20 µg/mL (FID) and 0.5–20 ng/mL (TOF MS). Selected curves from the TOF MS analysis are shown in Figure 3.

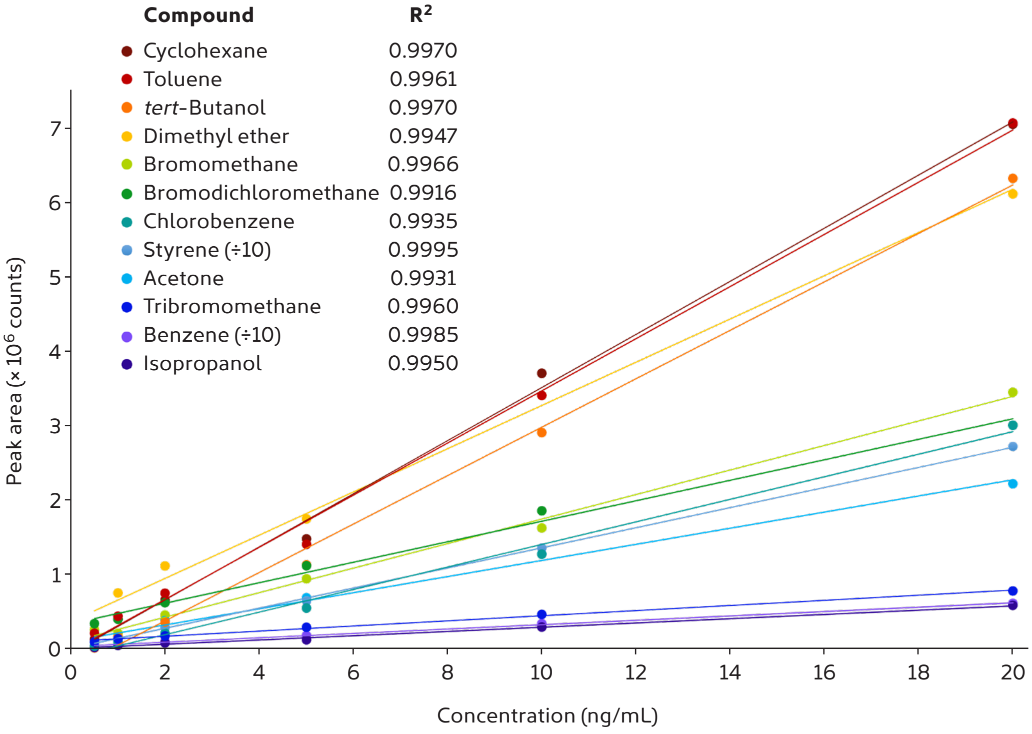


Figure 3

Linearity for a selection of target analytes with a variety of polarities and volatilities, using data acquired by TOF MS.

3. Repeatability

Method repeatability was assessed by monitoring the peak areas of five replicates at 5 µg/mL, prepared by the robotic autosampler by injecting 150 µL of a 500 µg/mL working solution of Mix B into 15 mL of water sampled using the flow cell. Figure 4 shows the excellent repeatability obtained for the FID analysis, with all RSDs <10%. The septum was also tested to ensure the system would remain leak-free during unattended operation – 300 replicate injections were successfully performed without any leaks occurring in the flow cell.

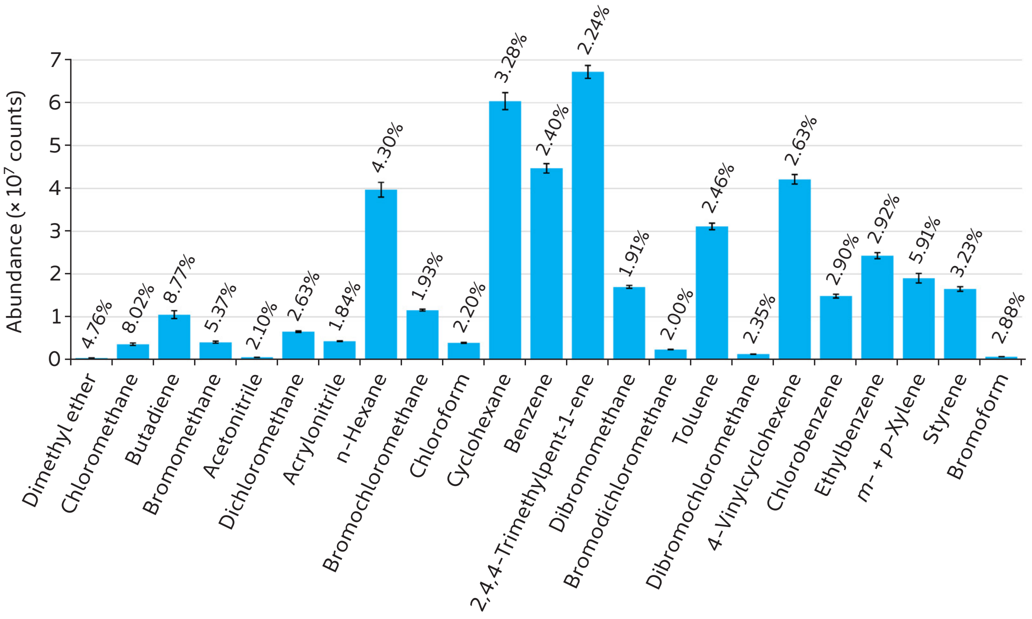


Figure 4

RSDs of target compounds in Mix B over five replicates at 5 µg/mL, using data acquired by FID.

The repeatability of the process of removing water from the flow cell was also assessed by weighing the headspace vial before and after dispensing 15 mL of water from the flow cell. Table 1 shows the high levels of accuracy (>98%) and precision (<0.03% RSD) achieved by the sampling robot, enabling confident unattended sampling using this approach.

Table 1

Determination of the precision and accuracy of the removal of the water sample by the sample preparation robot.

Run	Mass of vial (g)	Mass of vial + 15 mL water (g)	Mass of 15 mL of water (g)	Accuracy (%)
1	17.9059	32.6751	14.7692	98.461
2	17.7312	32.4928	14.7616	98.411
3	17.7320	32.5028	14.7708	98.472
4	17.8210	32.5929	14.7719	98.479
5	17.8126	32.5836	14.7710	98.473
6	17.8262	32.5966	14.7704	98.469
7	17.7857	32.5554	14.7697	98.465
8	17.7945	32.5626	14.7681	98.454
9	17.7808	32.5415	14.7607	98.405
10	17.7721	32.5422	14.7701	98.467
Mean ± standard deviation				**98.454 ± 0.026**

4. Automated workflows

The robotic tool change used in the system described allows automated switching of syringes, addition of standards, headspace sampling and injection, which together with the capacity for 180 × 20 mL headspace vials would allow ~1 week of unattended operation.

The flow cell used in the current study has capacity to handle six separate sample flows, allowing in-situ monitoring of multiple streams of waste-water effluent without the need for an operator to be present. Sample preparation can also be set to overlap, allowing the robotic autosampler to sample the water and generate the headspace while the GC is still running the previous sample. Figure 5 illustrates the significant time savings that are possible by using this 'prep-ahead function'.

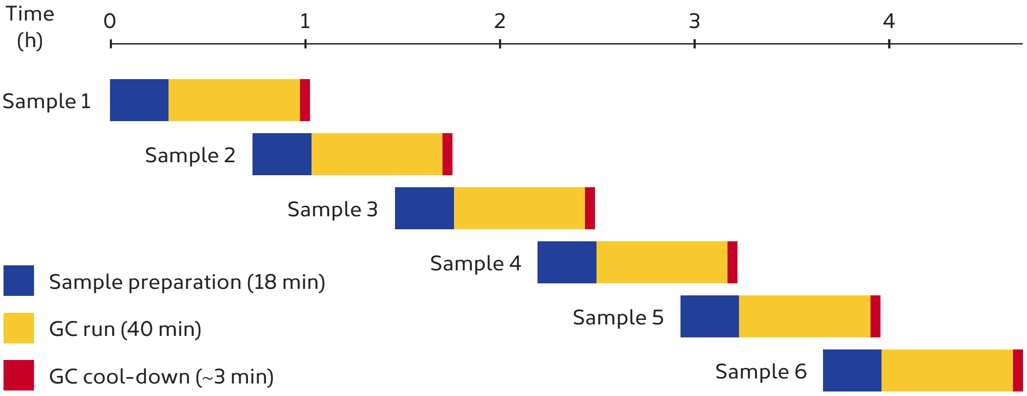


Figure 5

Schematic illustrating the time saving that can be made by using the autosampler's 'prep-ahead' function.

Cycle times were further reduced by the use of real-time data processing on the TOF-DS™ software platform. The global method in TOF-DS contains both instrument control and data processing parameters, which allows analyte peaks to be acquired, baseline-compensated, integrated, identified, quantified and exported (Figure 6) while the sample is still running, removing the need for an analyst to be continuously present on-site. If TOF MS detection is used, unknown compounds can also be automatically screened against commercial libraries (such as NIST or Wiley).

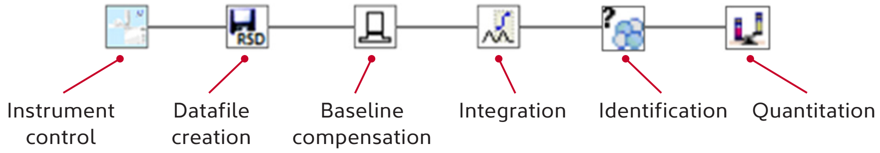


Figure 6
The icon-based method overview used in TOF-DS software.

Conclusions

This study has demonstrated that the system described offers:

- Fully automated sample abstraction, standard addition, headspace sampling and injection using robotic tool change.
- GC–FID for continuous in-situ monitoring and rapid response, and GC–TOF MS for confirmation of unknowns or emerging contaminants.
- Potential capacity for 180 × 20 mL headspace vials allows up to 1 week of unattended operation.
- Real-time data-processing for fast reporting of target compounds.
- Excellent reproducibility, with RSDs for all target compounds <10%.
- High accuracy (>98%) and precision (<0.03% RSD) using a sample preparation robot to collect the aqueous sample from the flow cell.

For more information on this application, or any of the techniques or products used, please contact SepSolve.